DEVELOPMENT OF NEW STEAM METHANE REFORMING MOBILE PLANT WITH MICRO-SCALE CATALYTIC CHANNELS

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A thesis submitted in fulfillment of the requirement for the award of the
Doctor of Philosophy of Mechanical Engineering

Faculty of Mechanical and Manufacturing Engineering
Universiti Tun Hussein Onn Malaysia

FEBRUARY 2019

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DEDICATION

Special Dedication to

Supiah Jamil@Jamin my beloved mother, you are everything to me,

Madon Jais my late beloved father, you are my inspiration,

Meine Leibe, I believe in you and me,

My family members that always love me,

My friends that always care for me,

Thanks you for always giving me encouragement to complete this study.

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ACKNOWLEDGEMENT

In the Name of Allah, the Most Gracious, the Most Merciful. I am so thankful to Allah S.W.T for giving me enough time, good health, spirit, and patience in order to complete this PhD's project. With the mercifulness of Allah, I am able to produce a lot of useful idea for this project.

I would like thank my supervisor, Assoc. Prof. Dr. Mas Fawzi bin Mohd Ali, for his continuous professional advices, useful guidance, inspiration, patience, financial aspects and enormous support in the effort to complete this project. Also, I would like to thank my co-supervisor, Prof. Dato' Ir. Dr. Abdul Wahab bin Mohammad for his advice and support during my study. I am would like to express my thankfulness to my beloved family, especially my beloved mother, Mrs. Supiah Jamil@Jamin, my beloved wife Mrs Nor Nadiah Harun, my daughter Ms Iffah Damia, my sons Rais Irfan Daniyal and Rais Iman Daaim for their prayers, support, patience, and motivation during my study. I am also grateful to both examiners for their brilliant ideas, advices and guidance to me

I am indebted to the Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia (UTHM) for their facilities, opportunity as well as financial aid provided in pursuing my research. I would like to thank the Ministry of Education Malaysia for supporting my scholarship under SLAB scheme and also for supporting this research project under the Fundamental Research Grant Scheme (FRGS) Vot 1421. I would like to dedicate my appreciation to all the lecturers and associates of the Faculty of Mechanical and Manufacturing Engineering, which involved in this project with their invaluable time, guidance and advice. Without their cooperation and sacrifices, this research would not be able to be completed and published. Especially to Mr. Muhamad Khairul Ilman bin Sarwani, Mr. Mzahar bin Abd. Jalal, Mr Asrul bin Bosiran and Dr. Shahrul Azmir bin Osman.

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ABSTRACT

The search for clean alternative energy sources is vital to feed the ever-increasing world energy consumption. It is widely accepted that hydrogen is the cleanest and abundant energy source of the future. Currently, more than 90% of world hydrogen production is made via catalytic steam methane reforming (SMR). A performing catalyst favors thermodynamic equilibrium that ensures good hydrogen selectivity. This research explores the potential of SMR yield intensification using experimental micro reactor and active noble metal catalyst (Rhodium aluminide and Ruthenium aluminide). For that purpose, a laboratory scale SMR test rig bench was designed, fabricated and developed. A new micro channel reactor with interchangeable catalyst modules for methane conversion process was set up and tested. The rig is able to provide evaluation of SMR experimental tests, such as catalyst performance, conversion rate and products at output stream, with controlled reactants steam to carbon ratio up to 5:1 and reaction temperature up to 700°C. The developed conventional and noble metal catalyst for this research, affirmed and proved that the combination of test rig bench and micro reactor managed to generate methane conversion according to the theory related to material catalyst. From this work, reaction temperature 650°C and steam to carbon ratio of 3:1 were found to yield the optimum methane conversion and hydrogen formation for the developed catalyst. Using such setup, the use of noble metal catalyst was able to reform methane to hydrogen within 1 minute from the start of reaction as compared to 60 minutes using conventional catalyst. It was found that the rate of reaction (methane disappearing rate) of $-r'_{CH_4}$ (mol CH_4 / g catalyst.s), for Rhodium aluminide yield the highest of 181.58, followed by Ruthenium aluminide with 154.39 and lastly Nickel aluminide of 1.32. The outcomes of this work has the potential to be scaled up for hydrogen production supply chain system of future fuel-cell electric vehicle transportation sector especially in any region with affordable natural gas price.

ABSTRAK

Peningkatan terhadap penggunaan sumber tenaga dunia telah mewujudkan keinginan untuk mencari sumber tenaga baharu sebagai langkah untuk menangani fenomena tersebut. Tenaga dari sumber hidrogen dipercayai menjadi calon utama tenaga masa hadapan. Lebih 90% penghasilan hidrogen ialah melalui proses tindak balas kimia *Steam Methane Reforming* (SMR). Sesebuah pemangkin membantu fasa keseimbangan termodinamik bagi SMR dan meningkatkan pengeluaran hidrogen. Kajian ini meneroka kebolehupayaan peningkatan hasil SMR dengan menggunakan reaktor skala mikro dan pemangkin *noble metal (Rhodium aluminide* dan *Ruthenium alumninide)*. Oleh itu, sebuah pelantar ujian proses SMR berskala makmal telah direka, dibina dan dibangunkan. Reaktor pada skala mikro dibina dan diuji dengan mempunyai ciri kebolehupayan menggunakan pelbagai jenis pemangkin. Pelantar ujian tersebut, menghasilkan data SMR seperti prestasi pemangkin, penukaran bahan tindak balas, produk terhasil dan dikawal pada nisbah mol bahan tindak balas sehingga 5:1 dan suhu tindak balas sehingga 700°C. Pemangkin dalam kajian ini, telah menunjukkan kesetaraan menurut teori asas SMR tatkala menggunakan pelantar ujian proses SMR dan reaktor skala mikro. Hasil kajian ini menunjukan bahawa suhu tindak balas 650°C dan nisbah mol bahan tindak balas 3:1 menghasilkan penukaran metana dan pembentukan hidrogen yang optimum. Berdasarkan tetapan berkenaan, penggunaan *noble metal* telah menunjukkan masa tindak balas penukaran metana kepada hidrogen seawal 1 minit pertama, berbanding pemangkin konvensional pada 60 minit yang pertama. Kadar tindak balas penukaran metana bagi setiap berat pemangkin dan masa, *Rhodium aluminide* telah menunjukkan nilai tertinggi iaini 181.58, diikuti *Ruthenium aluminide* dengan nilai 154.39 dan *Nickel aluminide* pada nilai 1.32. Hasil kajian berupaya menjadi platform fasa peningkatan kepada skala besar penghasilan hidrogen dimasa hadapan, terutama di dalam sektor pengangkutan khususnya bagi sistem rantaian pembekalan untuk kenderaan *fuel-cell* di kawasan yang mempunyai sumber gas semulajadi pada kadar harga mampu milik.

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LIST OF SYMBOLS AND ABBREVIATIONS

Al	Aluminum
AIGA	Asian Industrial Gas Association
Al_2O_3	Alumina oxide
C	Char
CH_4	Methane
CO	Carbon monoxide
CoGe	Cobalt Germanium
CO_2	Carbon dioxide
C-101	Condenser (101 = referring number of unit)
D-101	Dryer (101 = referring number of unit)
DME	Dimethyl ester
dV	Differential of reactor volume
dW	Differential of embedded catalyst weight inside reactor
dX	Differential of reaction conversion
Eqn.	Equation
$F^{o}_{CH_4}$	Molar flow rate of methane in feed
F_{CH_4}	Molar flow rate of methane at output
FIC 101	Flow Indicator Controller (101 = referring number of unit)
FT	Fischer Tropsch
F-101	Furnace (101 = referring number of unit)
H_2	Hydrogen
H-101	Steam generator (101 = referring number of unit)
ICE	Internal combustion engine
Ir	Irrididium
kg	kilogram
lph	liter per hour
lpm	liter per minute

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Mb/d	Million barrel per day
min	minute
ml	milliliter
MW	molecular weight
m^3	meter cube
NaOH	Sodium hydroxide
Na_2CO_3	Sodium carbonate
Ni	Nickel
NiO	Nickel oxide
Ni_3Al	Nickel aluminide
Ni_3Sn	Nisnite mineral
Ni/Al_2O_3	Nickel support alumina oxide
Pd	Palladium
PEM	Proton exchange membrane
PFD	Process Flow Diagram
PI 101	Pressure indicator (101 = referring number of unit)
PSA	Pressure swing absorber
PtGe	Platinum Germanium
PV	Process value
Pt	Platinum
P&ID	Process & Instrumentation Diagram
RBDPO	Refined Bleach Deodorized Palm Oil
Rh	Rhodium
Ru	Ruthenium
R-101	Reformer (101 = referring number of unit)
s	seconds
SOP	Standard Operating Procedure
SMR	Steam methane reforming
S-101	Separator (101 = referring number of unit)
SSC-101	Superheated steam converter (101 = referring number of unit)
SS304	stainless steel grade of 304
SS316	stainless steel grade of 316
TI 101	Temperature indicator (101 = referring number of unit)
V-101	Ball valve (101 = referring number of unit)

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W	weight % catalyst
WGS	Water gas shift
WHSV	Weight hourly space velocity
X_{CH_4}	Methane conversion
Å	Angstrom measurement
°C	degree Celsius
ΔH	Enthalpies
wt%	weight percent
2θ	Bragg reflection
µl	Micro liter
$\dot{\xi}_1$	Extent reaction for SMR equation
$\dot{\xi}_2$	Extent reaction for WGS equation
$(\dot{m})$	Steam mass flow rate
$\dot{n}_i$	Mole flow rate of species exit the reactor
$\dot{n}_{o,i}$	Mole flow rate of species into the reactor
$-r'_{CH_4}$	Rate of reaction (mol CH_4 /g catalyst.s)
$-r_{CH_4}$	Rate of reaction (mol CH_4 / dm^3.s)

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CHAPTER 1

INTRODUCTION

1.1 Research Background

It is reported the distribution of proved fossil fuel reserves from 1996 to 2016 had showed that the global oil demand grew by 1.6 million barrels per day and the oil reserves also increased at 1706.7 thousand million barrels in 2016, in consequences of both demand and supply trending (British Petroleum, 2017). It is believed that possibility of demand shortage will occur since fossil fuel is non-renewable. In addition to the cost and demand of fossil fuel energy, there was a significant environmental concern regarding petroleum fuel based usage. The recent analysis estimated that pollutants may be high enough to bear on public health and the environment in areas where 50% of develop country exist. Report by Daud, (2006) and Kamarudin et al., (2009) air pollution by transportation and industrial sectors are principally due to the using of fossil oil and natural gas as their source of fuel. Figure 1.1 shows the projection of production and demand of fossil fuel generally at world level and specifically at Malaysia level. Apparently, extreme depending on the fossil fuel lead to shortage of fuel energy sources and high potential of pollutant as the emission from combustion of the fossil fuel. Thus, in order to deal with these issues, there has been an effort to diversify energy supply for better energy efficiency and cleaner fuels. The utilization of renewable energy, capable to encounter the energy demand and to reduce the growth rate of greenhouse gases (GHG), which mainly concentrate of Carbon Dioxide (CO_2) as the emission from the fossil fuel usage. In Malaysia, renewable energy development is mainly focused on biomass-based power generation (BIOGEN), solar and hydrogen energy. It's believed that, the GHG impact from industrial sector and transportation should be reduced by 3.8% within 5 years

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(Daud, 2006, Holladay, et al., 2009; Kamarudin et al., 2009). The hydrogen energy at a smaller extent identified as most viable long term renewable energy as alternative fuel compared to the fossil fuel.

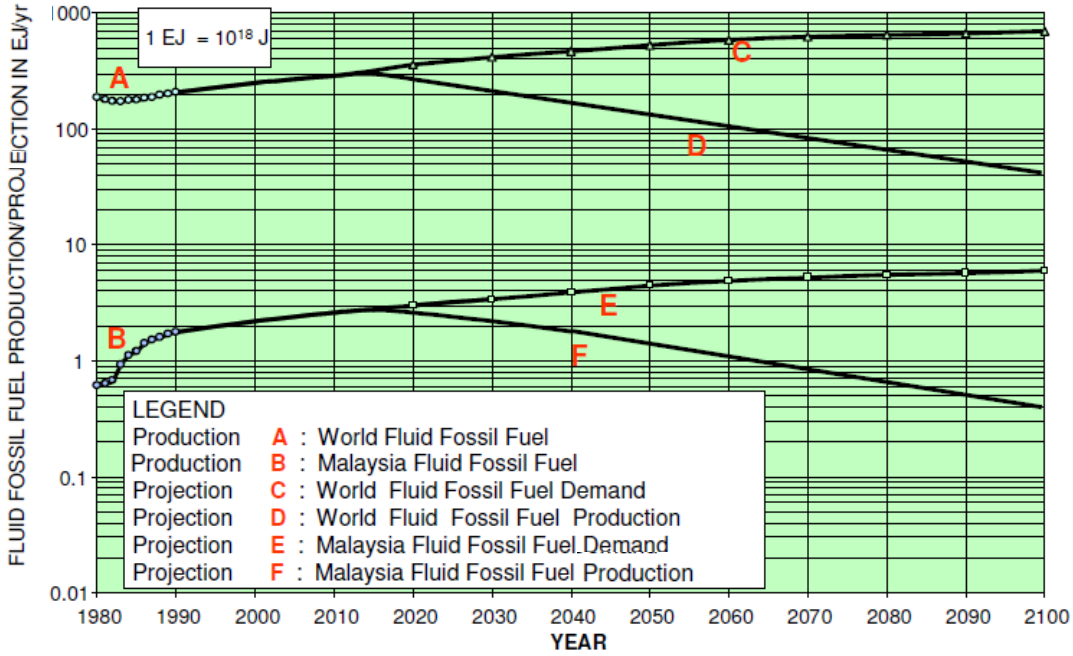

Figure 1.1 : Fossil fuel projection of production and demand (Daud, 2006).

It is widely accepted that hydrogen energy was among the clean, efficient and pollution free energy source in the future. The hydrogen energy becomes the main energy sources as fuel in fuel-cell system especially for the transportation sector. Besides that, this hydrogen is widely utilized as feedstock for food processing, chemical production and refining industries. Reported by Daud, (2006), Kamarudin et al., (2009) and Khan et al., (2010) the demand for hydrogen is expected to rapidly increase due its potential as major energy sources in the future. Figure 1.2 describes the route map of hydrogen energy, specifically in Malaysia which had been exhibited at International Seminar on The Hydrogen Economy for Sustainable Development, Reykjavik Iceland (Daud, 2006). The R&D of the hydrogen production and storage technologies has been started as early as 2002. This road map has become the baseline for hydrogen research area in Malaysia. This road map is mainly focused on transportation sector whereby the Hydrogen is used as energy sources for zero carbon emission fuel (Kamarudin et. al., 2009).

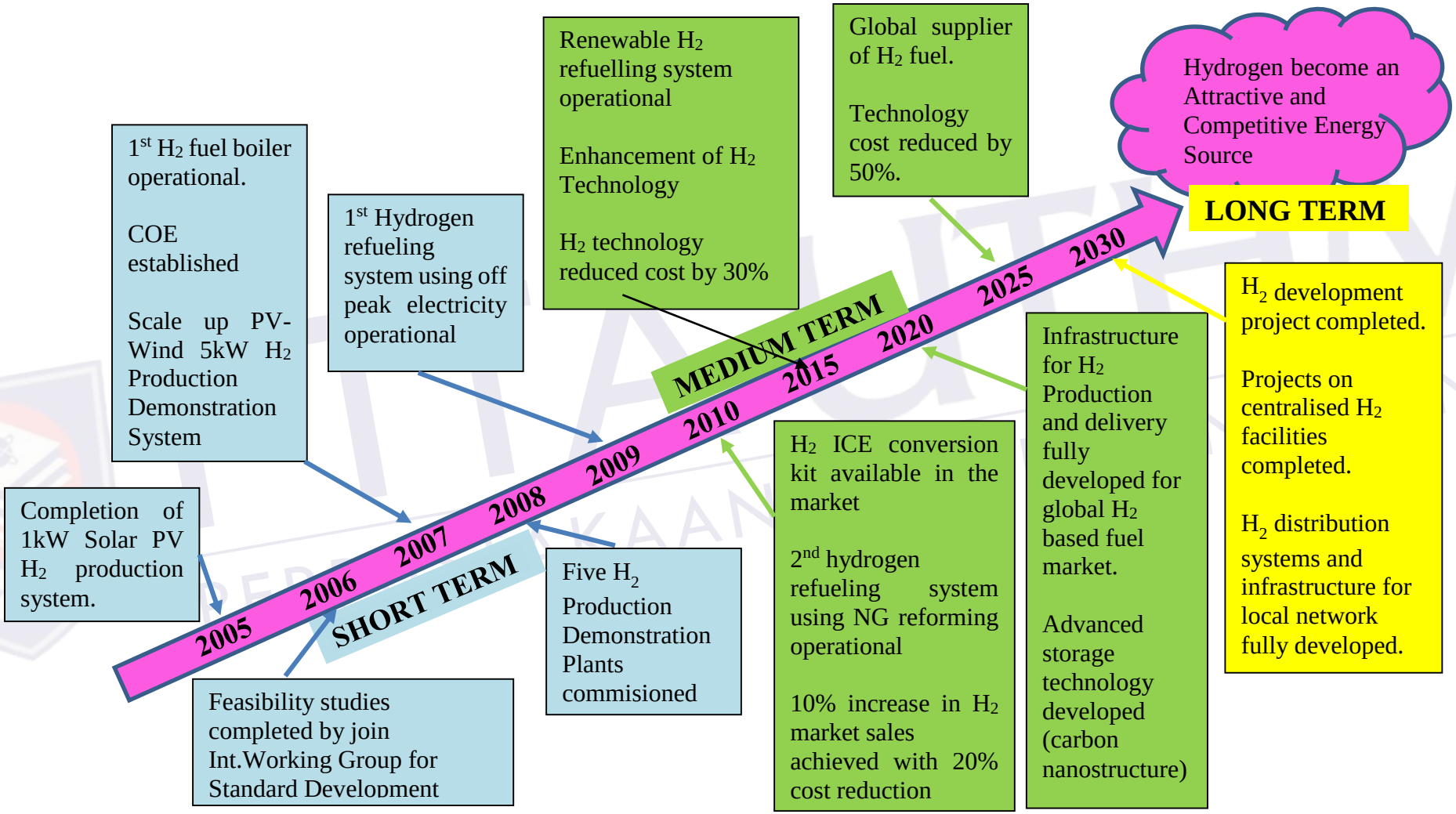

Figure 1.2: Hydrogen road map for Malaysia (Daud, 2006).

Established along the theory of stoichiometry equation for combustion reaction, Eqn. 1.1 shows any hydrocarbon produces carbon dioxide. The concentrated carbon dioxide leads to the greenhouse gas phenomenon and becomes worst polluted to the environment. Eqn 1.2 shows the combustion of hydrogen, which primarily produces water vapor. The equation demonstrate that the hydrogen is clean and zero carbon pollutant fuel (Sciazko et al., 2014; Udengaard et al., 2004; Verykios & Piga, 2000).

$$C_mH_n + \left(m + \frac{n}{4}\right)O_2 = \frac{n}{2}H_2O + mCO_2 \quad (1.1)$$

$$2H_2 + O_2 = 2H_2O \quad (1.2)$$

Reported by Holladay et. al., (2009) highlighted that the most developed and most used technology in hydrogen production was reforming of the hydrocarbon fuels, due its advantage such as highly efficient, low cost and already achieve commercial and long term stage in industry compare to non-reforming (biomass gasification, photolysis, electrolysis and etc). Furthermore, presently almost 96% of the world's hydrogen demand, including in Malaysia, is provided by traditional fossil fuels, and about half of it, comes from natural gas; which the main composition is methane (Bartels et. al., 2010; Bej et. al., 2013; Florin & Harris, 2007; Kamarudin et al., 2009; Udengaard, 2004). The production of hydrogen from various hydrocarbons, especially methane mainly comes from the chemical reaction process of catalytic reforming technologies which consist such as steam methane reforming, partial oxidation, and auto thermal reforming. Among these, catalytic steam methane reforming has the advantage of relatively low reaction temperature and high hydrogen content in the reforming products, and it is currently considered as the most cost efficient and highly evolved case of reforming for hydrogen production. Whereby, since the early 1950s, a considerable efforts have been set into the investigations of steam methane reforming (SMR) and its kinetics (Kamarudin et al., 2009; Khan et al., 2010; Wang et al., 2012; Wang et al., 2013).

The SMR is a strongly endothermic reaction inside tubular reactor with Nickel based catalyst, which requires external heating of the reactor tubes. This process is carried out by either the direct firing (as in radiant reformers) or by heat exchange with

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